Malachite pigment of spherical particle form

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Abstract

Malachite of spherulitic particle form is generally thought to be synthetic in origin. However, it could be mineral malachite formed by natural precipitation from flowing water. Agricola described a source of this type in Neusohl (Banská Bystrica, Slovakia) in 1546. This hypothesis was considered by evaluation of historical documentary sources on green pigment production in the Neusohl region, and the geological literature. Precipitation experiments imitating the natural conditions produced malachite of spherulitic form, and several wall paintings in Neusohl were found to contain spherulitic malachite. Evidence that these, and examples from Italian paintings, could be from a naturally precipitated source is presented.

Keywords

malachite, mountain green, schifergrün, spherulitic, Neusohl, pigment

Introduction

Numerous occurrences of spherulitic malachite ($Cu_2CO_3(OH)_2$) on easel and wall paintings, manuscripts and polychrome sculpture from north and south of the Alps have been published (Gettens and West Fitzhugh 1993, Naumova and Pisareva 1994, Martin et al. 1995, Wülfert 1996, Dunkerton and Roy 1996, Dunkerton et al. 2000, Trabska et al. 2000). Spherulitic malachite is generally thought to be synthetic in origin. However, on occasion it might be mineral malachite formed by natural precipitation from flowing water from a copper mine, or on tailings, as proposed in a recent paper (Heydenreich 2003). Agricola described a natural source of this type in *De Natura Fossilium* (1546), in Neusohl in the Carpathians. 'Green water' flowing from an ancient tunnel was collected in reservoirs in which 'chrysocolla' then precipitated. This was collected every year and sold as a pigment.

This paper considers the hypothesis further through analysis of paint samples containing spherulitic malachite, evaluation of documentary sources, and preparation of malachite by slow precipitation to simulate the natural conditions in Neusohl.

Mountain green from Hungary

Many documentary sources dating from the 17th to the 19th century state that the best mountain green came from Hungary (Marx 1687, Schmidt 1857), meaning the Neusohl region in the Carpathian Mountains in present-day Slovakia, previously known as the lower Hungarian ore-mining centre. The Neusohl ore deposits are mentioned in 13th century written sources, and in the 14th century Venetians and Florentines invested in the mines (Ratkoš 1971). In 1494 Jan Thurzo from Krakow and the Fugger family from Augsburg founded a trade company, leading to an enormous increase of production. After the Fugger left in 1546, mining continued with varying intensity until the 20th century.

In 1467 the *grünstollen* (green tunnel) was sold to Hans Constoffer for about 900 gilders, and in 1479 Veit Mühlstein received some income from green colour produced at Neusohl (Kachelmann 1867). In 1546 and 1556 Agricola described the production of *chrysocolla nativa* in Neusohl. The first German edition of *De Re Metallica* (1557) translates *chrysocolla* as *berggrün und schifergrün*. In 1584 production of *grine farb im Herrngrundt* (green pigment at Herrengrund) was given to Balthasar Lorenzen.[1] The pigment is documented at 55 florins per *Zentner* (one Viennese *Zentner* = 56 kg) in 1618 and 31 florins per *Zentner* in 1640.[2] Between 1697 and 1721 production of at least 153 *Zentner* 11 Pfund of green colour is documented from Sandberg and Lybethen mines (Vlachovic 1964), and between 1736 and 1745 a total of 203 *Zentner* 14½ Pfund of *Berggrün* was obtained at Herrengrund (Vozar 1983). A document of 1829 still reports an average annual production of 30–50 *Zentner* of *berggrün* at Herrengrund.[3]

The main mines were 8–12 km north of Neusohl between Herrengrund (Špania Dolina), Sandberg (Piesky) and Altgebirg (Staré Hory). An 18th century source mentions a *Grünstollen* at Sandberg, and a 19th century source a *Farbstollen* (colour tunnel) at Herrengrund (Zipser 1842). The villages were only 2 km apart, closely connected by the mines. Until about 1950 there were six sedimentation troughs 4–5m wide and 20 m long;[4] the green precipitate was taken to Banská Bystrica for electrolytic processing of copper. However, Sandberg no longer exists, as the decision was taken to further extract copper from the tailings on which the village stood.

Another green colour tunnel is documented in Lybethen (L'ubietová), 20 km east of Banská Bystrica, described in the 16th century as *ein fluss und stolln griener perckhfarben* (a river and tunnel of green mountain colour).[5] In 1524 this tunnel was owned by Juraj Königsberg and in 1532 it was sold to Jan Greimel and Cherubin Siebenburger. By 1534 the ore was no longer being mined, but pigment was still produced from the pit water (Slany 1982).

Natural precipitation of malachite in flowing water

Agricola's description states that: 'The water is collected in thirty large reservoirs, where it deposits the chrysocolla as a sediment, which they collect every year and sell [as a pigment]'. Ferber (1780) said that the water originated partly from the pit water of the mines located higher in the mountains and partly from rainwater draining through the tailings from the mine on which the houses of Herrengrund stood. In the 17th and 18th centuries, various authors tried to explain the formation of the green pigment; some thought that the water was sulphate-rich and thus the pigment might have been a form of copper sulphate (Delius 1773, Ferber 1780). Zipser (1842), however, stated that the solution was carbonate-rich, and different from the sulphate-rich water in the same area *(vitriolisches Cementwasser)* in which copper was extracted by means of iron.

The process that Ferber describes is acid mine drainage. The copper ores in this area are predominantly sulphides: tetrahedrite and chalcopyrite (Huber 1983). In the presence of water and oxygen, assisted by certain bacteria (genus *Acidithiobacillus)*, the sulphides can rapidly oxidize, causing the water to become acidic and sulphate-rich. Heavy metals from the ore, including copper, are leached out into the water. The subsequent processes depend on the balance between acid generation from oxidation of the sulphide minerals and the neutralization potential of the rocks that the water passes through or over; minerals such as calcium carbonate can buffer or neutralize the acidity. As the acid mine drainage is neutralized, the copper can precipitate out of the water, forming copper carbonate (malachite) and in some conditions other copper compounds such as copper sulphate (Huber 1983). In this region dolomite and calcareous rocks cover the ore-containing layers, and thus provide good conditions for the development of malachite. Analysis of green mineral collected recently from Sandberg found that it was composed of large quantities of malachite associated with dolomite.

In 1717 a delay in delivery of the green pigment from Herrengrund is documented.[6] This may be why some years later attempts were made to increase production; 'In 1752 a separate building was erected at high costs in which mountain green was to be produced by artificial precipitation from pumped cement water. However, this attempt by a dutch man (de Witt) faltered since the mountain green obtained by this method was unstable and turned black.' (Zipser 1817).

Despite these attempts, the method described by Agricola continued, the malachite forming simply as a result of the geological conditions. The term 'naturally precipitated malachite' seems appropriate, and Agricola must have considered it to be natural because he calls it *chrysocolla nativa*. Particles growing in water, with no constrictions, can develop a spherical form due to the splitting of crystals (Self and Hill 2003). This, and the fact that in the historic descriptions the precipitate was ready to use as a pigment after drying, makes it possible to hypothesize that spherulitic malachite could form.

Precipitation experiments

Experiments were done to investigate whether the precipitation conditions in Neusohl could produce spherulitic malachite. The silica gel technique was used, which is suitable for simulation of crystallization of sparingly soluble salts such as malachite in natural porous media, as is the case for precipitation occurring by circulation and reaction of fluids in sediments and sedimentary rocks. In this way the particle morphology of the precipitate produced under these conditions could be studied (Astilleros et al. 1998).

A silica gel prepared by acidification of Na_2SiO_3 solution with HCl (1N) was placed in the horizontal part of a U-shaped tube. The pH of the gel was adjusted to about 5.5. A sodium carbonate solution was placed in one of the verticals of the U-tube and a copper sulphate solution in the other.

Counter-diffusion of the reagents through the gel column leads to a progressive increase of the concentrations of CO_3^{2-}, Cu^{2+} ions and pH level along the gel column. As a result, supersaturation with respect to malachite rapidly increases. After about 10 days malachite nucleated in the middle of the gel column. Crystals were removed at different times to study the crystal morphology. The first crystals formed were small pale bluish-green spherules. A few days later the spherules had become larger and the colour had changed to dark green. The colour seems to be related to changes in the roughness of the surfaces and in the growth mechanisms. In the early stages the supersaturation levels are high, and the crystals grow by a continuous growth mechanism at a high rate, producing dendrites and spherulites with rough surfaces. As growth proceeds the solution becomes depleted in Cu^{2+}, CO_3^{2-} and OH^- so that the supersaturation level decreases. The crystals then grow at a lower rate and develop atomically smoother surfaces, resulting in crystals of a darker green colour.

These experiments suggest that spherulitic malachite formed in the way described in Neusohl could crystallize by the reaction of an acidic copper sulphate aqueous solution with neutralizing carbonate waters. In Neusohl the pigment was collected only once a year, suggesting slow growth which, as discussed above, is likely to produce malachite of large particle size and strong green colour. This could explain why the mountain green from Neusohl was highly valued.

Spherulitic malachite on paintings from the Neusohl area

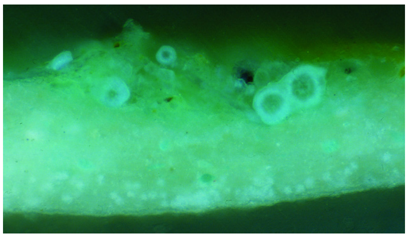

Figure 1. Cross section of a sample showing spherulitic malachite in a wall painting in a former merchant house in Neusohl

Crucial further evidence for this hypothesis came from the occurrence of spherulitic malachite in remnants of a wall painting in a former merchant house in the main square in Neusohl. The painting, which is thought to date from the late-15th century, is typical of the so-called 'green room' decoration common in the mining towns of this area. In a paint sample mint green spherulites of malachite are visible, some of them conjoined (Figure 1). In the back-scattered image in the scanning electron microscope (SEM) it can be seen that the ends of the radiating needles making up the particles have created slightly feathered edges, which scatter light, giving a lighter green halo (Figure 2). There are also a few angular particles of posnjakite ($Cu_4(SO_4)(OH)_6{\cdot}H_2O$), some black copper sulphide, and needle-shaped particles of potassium aluminium silicate. In a second sample, as well as many round particles, there is also a large conglomerate of parallel columnar particles that has the appearance of a row of teeth (Figure 3). Each tooth-shaped particle is composed of splayed needle-shaped crystals. It seems unlikely that this type of conglomerate would be present in artificially produced malachite. The presence of silicates also suggests that it was formed in a natural environment, and both posnjakite and dolomite are known to be

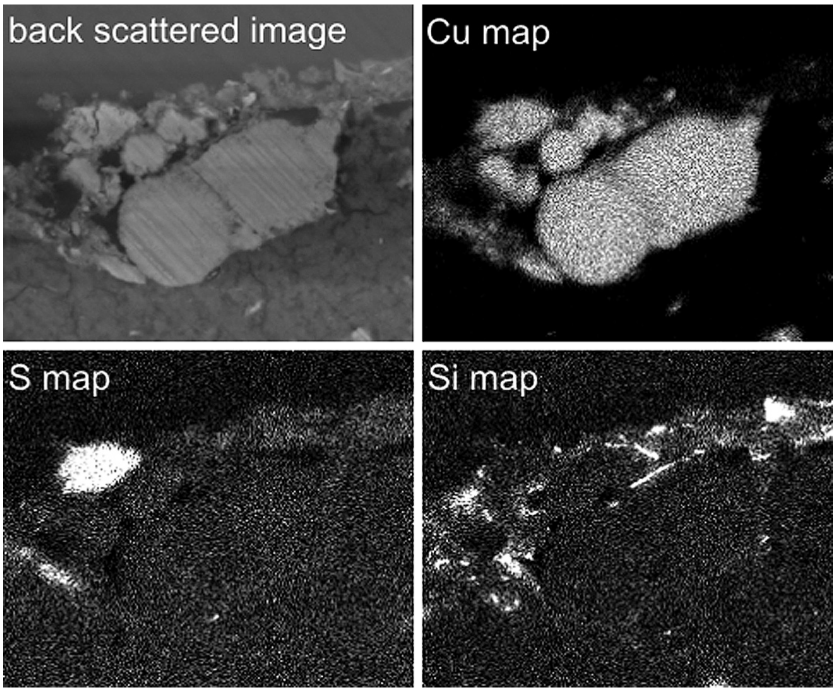

Figure 2. Back-scattered image of the cross section in Figure 1, focusing on two conjoined particles on the right, with EDX maps for copper, silicon and sulphur

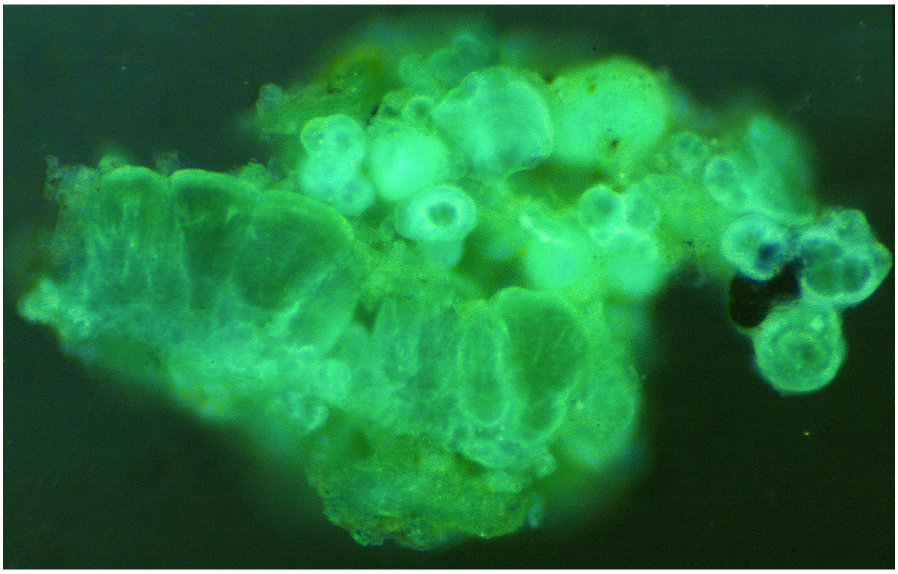

Figure 3. Second cross section from a wall painting in a former merchant house in Neusohl, showing a tooth-like conglomerate of particles

present on the hills near Neusohl. In addition, it seems unlikely that artificial malachite would be used for a wall painting in Neusohl, within reach of the locally produced *chrysocolla nativa* described by Agricola.

Spherulitic malachite has also been found on other paintings located close to Neusohl (Table 1), including a painting in Zvolen Castle from 1491–1510 when the castle was owned and renovated by Jan Thurzo. On two more 15th century wall paintings, in churches in villages around 150 km from Banská Bystrica, a mixture of spherical and angular particles of malachite were seen and two 18th century examples are listed in the Table 1.

Trade from the Carpathians

As well as being used by local masters, the pigment produced in the Neusohl region was sold to many places in Europe closely linked with the copper trade.

Table 1. Occurrences of spherulitic malachite on paintings from Slovakia

Location of painting	Description and date	Description of pigment
Banská Bystrica, former merchant house at 23 SNP Square.	Fragments of a wall painting in a room on the ground floor, late 15th century.	Many perfect spherules of malachite (confirmed by Raman microscopy), some conjoined, 15–35 μm in diameter. Some posnjakite (copper sulphate, identified by Raman) and needle-shaped particles of potassium aluminium silicate (Si, Al, K, small Mg, Fe detected by EDX).
Zvolen Castle (25 km south of Banská Bystrica).	Wall painting, vault of a passage in the north wing. Probably 1491–1510.	Spherulitic malachite seen in samples from four areas of the painting. Average diameter 5–10 μm, but also some up to 40 μm in diameter.
Chyžné village (about 150 km east of Banská Bystrica), Roman Catholic Church of the Annunciation of Our Lady.	Wall painting, east wall of presbytery: green from St Peter's drapery, around 1470–80.	Mixture of angular and round green particles. Mostly around 5–20 μm diameter, one round particle 50 μm diameter. The larger grains have a darker colour.
Turňa nad Bodvou village (about 160 km east of Banská Bystrica), Roman Catholic Church of the Assumption of Our Lady.	Wall painting, sedilia; green background behind the angel, 15th century.	Mixture of angular and round green particles 5–50 μm diameter.
Gemerský Jablonec village (about 90 km southeast of Banská Bystrica), Roman Catholic Church of St Abdon and Sennen.	Wooden painted ceiling, green from floral ornament, 1703.	Amorphous green mass, with darker green round particles of malachite 5–20 μm diameter.
Bratislava (about 200 km southwest of Banská Bystrica), restaurant 'Velki Frantiskani', Frantiskanske square.	Wall paintings in a few rooms, some gothic, some renaissance. Spherulitic malachite found in the renaissance decoration.	Mixture of angular and round green particles 5–20 μm diameter.
Ludanice village (about 120 km south-west of Banská Bystrica), Roman Catholic Church of the Holy Trinity.	Cornice of the architecture of the rococo wooden altar, 1759.	Spherulitic malachite particles, 5–15 μm diameter.

In the 14th century large quantities of the metal were transported northwards to Flanders and south to Venice, the most important customer of the period (Ratkoš 1971). In the second decade of the 16th century, the war the Emperor waged with Venice impaired copper export to the south. Instead, copper was traded by the Fugger mainly through Wroclaw (Breslau) and Leipzig or Gdansk to Germany and Antwerp. Two hundred and sixty-four carriages loaded with up to 2 tonnes of copper from Neusohl passed through Leipzig in 1524 (Straube 1997). Leipzig, Frankfurt and particularly Antwerp became important trading centres of Hungarian copper in the 16th century. In the 17th century there was a growth in trade towards Amsterdam (Vlachovic 1977).

Trade of fine Hungarian mountain green (*Bergrün*, *fein ungarisch*) at 50–80 florins for one *Zentner* is documented at the Frankfurt fair between 1624 and 1627 (Dietz 1970). At the Leipzig markets Cranach bought the green pigment *Schifergrün*, a name used by Agricola for the pigment from Neusohl; spherulitic malachite has been found on a ceiling painting at Colditz Castle, where Cranach had been responsible for the decoration (Heydenreich 2003). In the 18th century the pigment from Herrengrund was sold to Vienna at 100 gilders per *Zentner* (Ferber 1780).

Spherulitic malachite in paintings from elsewhere in Europe

Malachite with a spherical particle form has also been found on paintings from Italy, Austria, Poland and Germany. Given the trade routes to many different parts of Europe, it seems possible that artists could have used naturally precipitated malachite from Neusohl. Alternatively, the spherulitic malachite could have come from another source where the pigment was being produced in the same way, and it is of course possible that it is artificial in origin. The components found in the pigment on the wall painting in Neusohl were not sufficiently unusual to distinguish it from malachite from other sources. However, several of the samples from paintings from elsewhere in Europe were similar in composition, and in others there were features that pointed towards a natural source.

The samples examined by scanning electron microscopy–energy dispersive X-ray spectrometry (SEM-EDX), Raman microscopy and X-ray diffraction were from 15th and 16th century paintings (Table 2). In general, the spherical malachite is large in particle size, which might suggest that the pigment formed over a long period, as it did in Neusohl. The proportion of spherical malachite in the samples is variable. Often there are angular particles as well, and many particles are rounded but not spherical. In some samples, such as that from Benozzo Gozzoli's *Altarpiece*, most of the malachite appears round in normal light, but in the back-scattered image in the SEM it is clear that only a few particles are perfect spheres. Some chlorine was detected by EDX in the spheres, and there are other small particles containing more chlorine, which are probably a copper chloride. This was common in the samples analysed. Some silica is also present, together with needle-shaped particles of potassium aluminium silicate, perhaps an indication that the pigment has formed in a natural environment.

Table 2. Summary of analysis of examples of spherulitic malachite in Italian paintings from the National Gallery, London

Artist, painting title and date	Description of samples	Results of analysis (EDX in the SEM, Raman microscopy)
Cosimo Tura, *An Allegorical Figure* (NG 3070, 1455–60).	Shadow of the interior of the cave. High proportion of large spherical particles of malachite, some angular particles. Olive green particles, some tabular and some rounded. Some blue particles.	Round and angular green particles contain Cu only (malachite). Reasonable quantity of silica (Si only) and potassium aluminium silicate (Al, Si, K, small Mg, Fe). Some dolomite (Ca, Mg). Darker green particles of posnjakite (Cu, S by EDX, Raman). Small amount of azurite (Raman).
Benozzo Gozzoli, *The Virgin and Child Enthroned with Angels and Saints* (NG 283, 1461–2).	Green of landscape. Mint green closely packed rounded particles of even size. In the back-scattered image in the SEM, can see that only a few particles are perfect spheres.	Mostly malachite (Cu only detected). Small amount of copper chloride present, some silica (Si only) and some needle-shaped potassium aluminium silicate (Al, Si, K, small Mg, Fe).
David Ghirlandaio, *The Virgin and Child with Saint John* (NG 2502, 1490–1500).	Dull brownish green of distant hillside. Rounded rather pale bluish-green particles. Some spherical particles. Natural zinc-containing malachite used for the lining of the Virgin's robe.	Mostly malachite (Cu only detected). Small amount of copper chloride also present. Small impurity of Sb in some of the malachite particles. Some silica (Si only) and potassium aluminium silicate (Al, Si, K, small Mg, Fe).
Sandro Botticelli, *Three Miracles of Saint Zenobius* (NG 3919, about 1500).	Dark green sleeve of the beggar at the right edge of the painting. Coarse pigment, giving the paint a gritty texture. One or two spherical particles, the rest are rounded.	Cu only in the green particles, sometimes with a small impurity of Cl. Potassium aluminium silicate (Al, Si, K with small Fe, Mg).
Sandro Botticelli (workshop of), *The Virgin and Child with Saint John* (NG 2497, 1482–98).	Green lining of the Virgin's cloak. Very round particles in a translucent yellow-brown matrix of discoloured medium and colourless associated minerals. Verdigris in the green landscape.	Cu only in the green particles, sometimes with a small impurity of Cl. Small amount of copper chloride also present. Potassium aluminium silicate (Si, Al, K, small Fe, Mg).
Sandro Botticelli (workshop of), *The Virgin and Child with a Pomegranate* (NG 2906, about 1480–1500).	Green of landscape. Rounded mint green particles in a yellow-brown matrix of discoloured medium and colourless associated minerals.	Cu only in the green particles, sometimes with an impurity of Cl. Small amount of copper chloride also present. Small impurity of Sb in some of the malachite particles. Some silica (Si only).
Matteo di Giovanni, *Christ Crowned with Thorns* (NG 247, 1480–95).	Green paint from the crown of thorns. Some perfect spheres (13–17 μm), some azurite and some variation in the shade of green of the particles.	Green particles contain only Cu. In a few of these are small but significant impurities of Zn, Sb and As. Some silica (Si only), some calcium carbonate (Ca only) and some potassium aluminium silicate (Al, Si and K with small Mg and Fe). Darker green particles of posnjakite (Cu, S by EDX, Raman). Small amount of azurite (Raman).
Matteo di Giovanni, *Saint Sebastian* (NG 1461, probably 1480–95).	Green of background foliage. Some very round green particles, some more angular.	Cu only in the green particles, sometimes with a small amount of Cl. Some silica (Si only). Green particle containing Sb, Cu, Al, red-brown impurity containing Fe, Cu, As, Bi, colourless particle containing Cu, Zn, Sb and a little As, red-brown particle containing Fe, Cu, Sb.

Silica and potassium aluminium silicate were found associated with spherulitic malachite in all of the Italian paintings examined. In a sample from Cosimo Tura's *Allegorical Figure*, one of the silicaceous particles is coated with malachite, as if it has nucleated on the silicate particle, proving that the silicate was present when the malachite was formed (Figures 4 and 5). Malachite nucleated on a silicaceous particle was also seen in three paintings by Botticelli or his workshop, and one by David Ghirlandaio. In a sample from Botticelli's *Three Miracles of Saint Zenobius*, a tabular particle of silicate appears in the back-scattered image as a darker grey core inside a lighter grey particle (Figures 6 and 7). This is perhaps

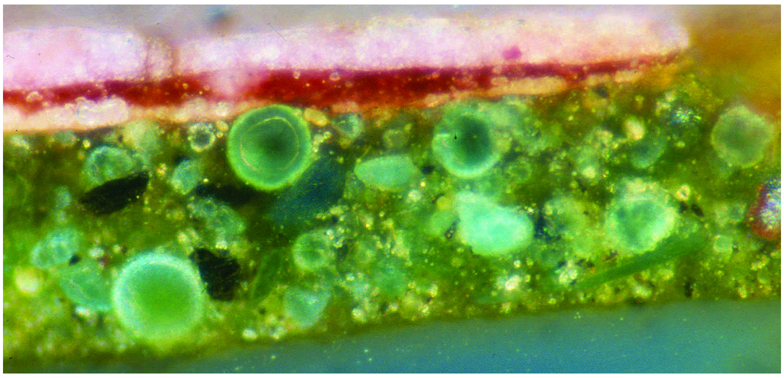

Figure 4. Cosimo Tura, Allegorical Figure (NG3070), shadow of the interior of the cave, where pink paint lies over the malachite-containing green landscape

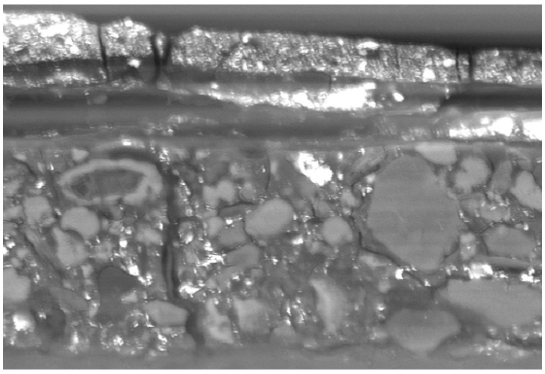

Figure 5. Back-scattered image of part of the cross section in Figure 4, showing a malachite halo around a silicate particle at the left

the best evidence that the spherical malachite in these samples comes from a natural environment.

In several of the Italian examples, as in the sample from Neusohl, a little copper sulphate was found with spherulitic malachite. In the sample from Cosimo Tura's *Allegorical Figure*, large green spherical particles of malachite are visible, together with tabular olive green particles of posnjakite. There is also some azurite and more angular malachite, together with silica, silicates and a little dolomite. The same combination was confirmed on Matteo di Giovanni's *Christ Crowned with Thorns*. It seems likely that these are all part of the 'mountain green' pigment and not mixed together on the artist's palette. It was typical of the Italian works examined in that there were only a few particles of spherulitic malachite in the sample. Here though, the round particles were smaller and the proportion of angular malachite was higher than in the painting by Cosimo Tura. A small amount of antimony, zinc and arsenic was detected in some of the angular malachite particles, which are not uncommon as impurities in copper deposits. The major component of the green pigment in Matteo di Giovanni's *Saint Sebastian* is malachite (spherulitic and angular). However, associated with the malachite are particles of several different exotic copper minerals, including a red-brown particle containing Fe, Cu, As and Bi, a large colourless particle containing Cu, Zn, Sb and a little As, and a pale green particle containing Cu, Sb and Al. It seems unlikely that these complex minerals could form during preparation of artificial malachite, and natural copper minerals containing these combinations of elements do exist.

Hungarian mountain green (from Neusohl) was valued for its colour, but it is difficult to assess the colour of the pigment in these paintings because the paint is dark brown due to discoloration of the binding medium. The colour can still be seen under the microscope but is variable; sometimes it has a bluish-green hue, while it can be more yellow-green. In some paintings both spherulitic and

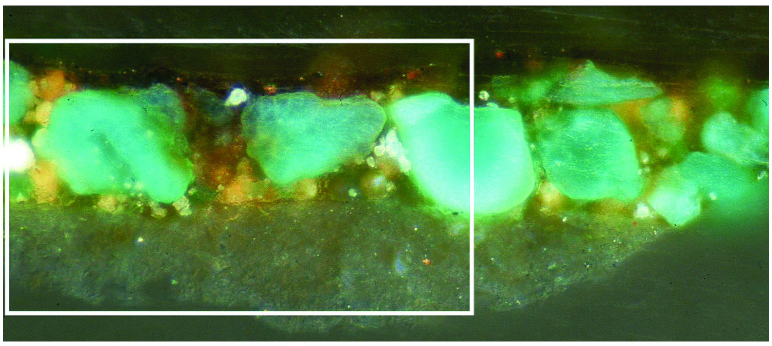

Figure 6. Botticelli, Three Miracles of Saint Zenobius (NG3919), cross section from a green drapery, showing large rounded particles of malachite

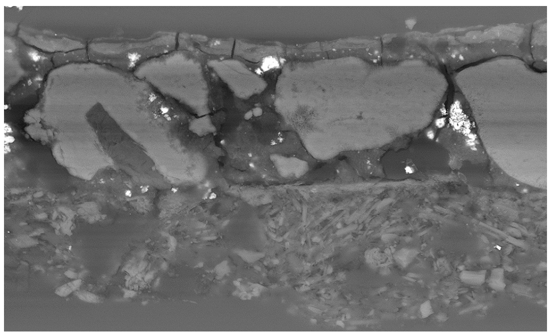

Figure 7. Back-scattered image of the part of the cross section in Figure 6 marked with the white box, showing a large malachite particle (on the left) that has a tabular potassium aluminium silicate particle at its core

angular malachite have been used, in different areas, suggesting that there was a difference in colour. Generally, rounded malachite was used for foliage and angular malachite for draperies, which might suggest that the rounded malachite was more grass green in colour.

It is difficult to prove with certainty that the spherulitic malachite in these paintings is from a natural source. However, the uncertainties of the conditions of natural precipitation could explain the presence of a mixture of copper minerals of different particle forms, some of them quite exotic. The presence of significant amounts of silicate also points towards formation of the pigment in a natural environment. At the very least, the study of how green pigment was formed at Neusohl provides an alternative possible origin for spherulitic malachite. The existence of naturally precipitated malachite, as well as artificial malachite, might also explain the difference between the spherulitic malachite in 15th and 16th century paintings, which is often of large particle size and strong green colour, and the smaller paler artificial malachite (green verditer) seen in later paintings.

Conclusion

The production of a copper-containing pigment by natural precipitation from flowing water at Neusohl was described already in 1546 by Agricola. Consideration of documentary sources on this copper mining area suggests that the process was essentially the neutralization of sulphate-rich acid mine drainage by carbonatic rocks, with subsequent precipitation of malachite. The precipitation experiments designed to imitate these natural conditions suggested that the malachite could have a spherulitic particle form, as did the occurrence of spherulitic malachite on paintings in and around Neusohl. The experiments also showed that if the pigment precipitated slowly (as it must have done at Neusohl because it was only collected once a year), larger spherules of a better colour were formed. The pigment from Neusohl (Schifergrün or Hungarian mountain green) was exported and was considered to be of good quality, which would suggest that it was of a desirable strong green shade.

Acknowledgements

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Notes

1 ŠUBA (State Mining Archive Banská Štiavnica), HKG, R 16.oct.1584.
2 ŠUBA, HKG, Resolutions, Prothocoll 1001-1699, 209.
3 Bauer, J, *Generelle Darstellung des K.K. Herngrunder Bergwerkes*, manuscript, ŠUBA, Inv. 9099, I225.
4 Personal communication Mr Cillik.
5 Municipal Archive Banská Bystrica AMBB-133/11, personal communication Peter Kalus.
6 ŠUBA, HKG, Berichte - Protocoll 1566-1734, 17.

References

Agricola, G, 1546, *De Natura Fossilium Libri X*, Basle, Fraustadt, G (trans.) Berlin, 1958, 81.

Agricola, G, 1556, *De Re Metallica Libri XII*, Basle 496, 470.

Agricola, G, 1557, *Vom Bergkwerck*, Basle, 482.

Astilleros, J M, Pina, C M, Fernández-Díaz, L and López-Andrés, S, 1998, 'Malachite crystallisation in a diffusing-reacting system', *Crystal Research and Technology* 33 (1), 51–57.

Delius, C T, 1773, *Anleitung zu der Bergbaukunst*, Vienna, 426.

Dietz, A, 1970, *Frankfurter Handelsgeschichte, II*, Glashütten, 342.

Dunkerton, J, and Roy, A, 'The materials of a group of late fifteenth-century Florentine panel paintings', *National Gallery Technical Bulletin* 17 (1996) 20–31.

Dunkerton, J, Foister, S, and Spring, M, 2000, '*The Virgin and Child Enthroned with Angels and Saints* attributed to Michael Pacher', *National Gallery Technical Bulletin* 21, 4–19.

Ferber, J J, 1780, *Physikalisch-Metallurgische Abhandlungen über die Gebirge und Bergwerke in Ungarn*, Berlin, 166–168.

Gettens, R J and West Fitzhugh, E, 1993, 'Malachite and green verditer' in Roy, A (ed.), *Artists' Pigments: A Handbook of Their History and Characteristics 2*, Washington, 183–202.

Heydenreich, G, 2003, 'A note on Schifergrün', *Studies in Conservation* 48, 227–236.

Huber, S and Huber, P, 1983, 'Herrengrund', *Lapis* 5, 19–29.

Kachelmann, J, 1867, *Geschichte der ungarischen Bergstädte und ihrer Umgebung*, Schemnitz, 95.

Naumova, M M and Pisareva, S A, 1994, 'A note on the use of blue and green copper compounds in paintings', *Studies in Conservation* 39, 277–283.

Martin, E, Duval, A and Eveno, M, 1995, 'Une famille de pigments verts mal connue', *Techne* 2, 76–79.

Marx, J J, 1687, *Materialist und Specerey-Händler*, Nuremberg, 79.

Ratkoš, P, 1971, 'Das Kupferwesen in der Slowakei vor der Entstehung der Thurzo-Fuggerischen Handelsgesellschaft' in Bog, I, *Der Aussenhandel Ostmitteleuropas 1450–1650*, Köln, 585–587.

Schmidt, C H, 1857, *Vollständiges Farbenlaboratorium*, Weimar.

Self, C and Hill, C, 2003, 'How speleothems grow: an introduction to the ontogeny of cave minerals', *Journal of Cave and Karst Studies*, August, 132.

Slany, J, 1982, 'Lubietovska med v 16 a 17 Storoci', in Soka, M (ed.), *Stredne Slovensko*, Osveta, 168–182.

Straube, M, 1997, 'Die Stellung Mitteldeutschlands im europäischen Handelsverkehr zu Beginn der Neuzeit', in Donnert, E (ed.), *Europa in der Frühen Neuzeit*, Köln, 115–116.

Trabska, J, Gawel, A and Trybalska, B, 2000, 'Some green and blue synthetic pigments: malachite and alkaline copper chlorides', *Biuletyn Informacyjny Konserwatorórow Dziel Sztuki* 3, 74–80.

Wülfert, S, 1996, 'Materialbezogene Untersuchungen an vier Tüchleinmalereien', *Riggisberger Berichte* 4, 169.

Vlachovic, J, 1964, *Slovenska med v 16 a 17 Storoci*, Bratislava, 239.

Vlachovic, J, 1977, 'Die Kupfererzeugung und der Kupferhandel in der Slowakei vom Ende des 15 bis zur Mitte des 17 Jahrhunderts', in Kellenbenz, H (ed.), *Schwerpunkte der Kupferproduktion und des Kupferhandels in Europa 1500–1650*, Köln, 154.

Vozar, J (ed.), 1983, *Das Goldene Bergbuch*, Bratislava, 210, 228.

Zipser, C A, 1817, *Versuch eines topographisch-mineralogischen Handbuches von Ungern*, Oedenburg, 101.

Zipser, C A, 1842, *Neusohl und dessen Umgebungen*, Ofen, 53.